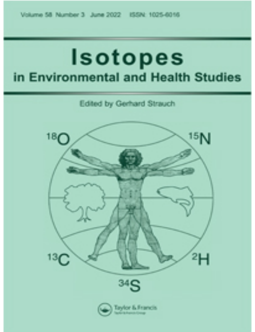

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Assessing land use influences on isotopic variability and stream water ages in urbanising rural catchments

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ABSTRACT

Stable water isotopes are invaluable in helping understand catchment functioning and are widely used in experimental catchments, with higher frequency data becoming increasingly common. Such datasets incur substantial logistical costs, reducing their feasibility for use by decision makers needing to understand multi-catchment, landscape-scale functioning over a relatively short period to assess the impact of proposed land use change. Instead, reconnaissance style surveys (high spatial resolution across the landscape at a lower temporal frequency, over a relatively short period) offer an alternative, complementary approach. To test if such sampling could identify heterogeneities in hydrological functioning, and associated landscape controls, we sampled 27 stream sites fortnightly for one year within a peri-urban landscape undergoing land use change. Visual examination of raw data and application of mean transit time and young water fraction models indicated urbanisation, agriculture and responsive soils caused more rapid cycling of precipitation to stream water, whereas mature forestry provided attenuation. We were also able to identify contiguous catchments which functioned fundamentally differently, meaning their response to land use alteration would also be different. This study demonstrated how stable water isotopes can be a valuable, low-cost addition to tools available for environmental decision makers by providing local, process-based information.

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1. Introduction

Stable water isotope signatures in precipitation (i.e. deuterium and oxygen-18 – hereafter δ^2H and $\delta^{18}O$, respectively) exhibit pronounced short-term and seasonal variation [1], with the damping and lagging of these variations in stream water being indicative of how long water takes to move through a catchment and the associated mixing with

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stored water [2]. Utilisation of tracer-based knowledge has been widely applied to gain a better understanding of catchment functioning, dominant flow pathways, storage volumes and water ages [3–9]. These hydrological processes and characteristics are, in part, governed by land use, with land use change via urbanisation or conversion to intensive agriculture becoming increasingly ubiquitous, so impacting, to varying degrees, observed hydrological regimes of a given area (cf. [10–12]).

When assessing the level of hydrological impact (and possible mitigation) of proposed land use change, decision makers should be guided, in part, via evidence derived from data collection campaigns. Such campaigns must yield sufficient information which can highlight, and attribute possible explanation for, heterogeneities in hydrological function across landscapes with diverse land use and thus enable comparisons between current and proposed land uses to be considered in a hydrological context. Moreover, such campaigns are typically limited in both time and resources due to multiple other factors needing to be considered within an environmental impact assessment, for example, possible impacts to water supply, air quality and biodiversity due to the proposed changes [13]. These resource limitations usually mean the collection of isotopic data is not considered viable within hydrological impact assessments, especially given recent research trends to focus on higher frequency data [14], often collected in single experimental catchments with auxiliary hydrometeorological and hydrometric information. However, if the outstanding potential of isotopes to unravel hydrological functioning could be satisfactorily exploited in a reconnaissance style survey (high spatial resolution across the landscape at a lower temporal frequency, over a relatively short period) then such data could provide a valuable auxiliary evidence base to inform environmental decision makers. How to effectively balance resource efficiency with derived isotope dataset information content is an open question that likely varies in different geographical environments and has no clearly defined answer [15].

However, in specific fields of applied hydrological research relatively short-term reconnaissance style isotope surveys have provided datasets with valuable information content. For example, Jameel et al. [16] recently demonstrated the ability of stable water isotopes to be used as a reconnaissance tool to investigate urban water supply system dynamics. Grimmeisen et al. [17] sampled for stable isotopes using a low-frequency approach, over approximately 22 months, at multiple sites to investigate the partitioning and mixing of urban surface and subsurface waters, concluding that the limited dataset provided evidence which helped achieve their research objectives. Similarly, Vystavna et al. [18] sampled six groundwater wells and precipitation on a monthly basis during – though not throughout in the case of groundwater – a two-year period, as well as tap water from two drinking supply schemes at a lower frequency, to investigate sources of groundwater recharge and for variability of tap water isotopic compositions. They demonstrated how such data, in conjunction with other hydro-chemical parameters, could successfully be used as a tool for urban water resource management. Gabor et al. [19] undertook various sampling approaches, including six synoptic sampling campaigns and storm event sampling over two years to successfully determine how urban influence impacted hydrological processes of a third-order catchment. Finally, Hepburn et al. [20] undertook three groundwater sampling campaigns over a one-year period from 36 sites to assess the sources of groundwater recharge and residence times in an area of

Australia which had major land redevelopment planed. They then discussed the important practical implications for the proposed redevelopment.

Therefore, to assess the benefits and drawbacks of reconnaissance style isotope data collection for use by environmental decision makers considering impacts of land use change in the UK, we sampled stream water for isotopic analysis roughly fortnightly, over one year, in 27 catchments within and surrounding a rapidly growing town in NE Scotland. These data were used in conjunction with local daily precipitation data and other readily available secondary datasets to identify whether heterogeneities in hydrological functioning and associated landscape controls could be identified. More specifically, we addressed the following research objectives:

(1) To identify if spatially extensive, low frequency stream water isotope sampling can be used with simple lumped models as a reconnaissance tool to identify differences in catchment hydrological functioning across a landscape.
(2) To test if any dominant local landscape controls on such differences can be identified in an area with rapidly changing land use.
(3) To evaluate the pros and cons of reconnaissance style isotopic surveys to aid environmental decision makers given insights from addressing objectives 1 and 2.

2. Study area

The study area (Figure 1) in NE Scotland encompassed the town of Banchory and its surrounding rural hinterland. The area is experiencing relatively rapid and diverse land use change. The town, an important commuter settlement for the city of Aberdeen, which has experienced rapid growth since the 1980s, continues to expand from its current size (~8.1 km^2) and population (~6000 [21]) into the predominantly commercially afforested and intensively managed agricultural areas of the surrounding countryside. Forested areas are reaching maturity given their planting post second world war, meaning current *Picea sitchensis* and *Pinus sylvestris* dominated areas could soon be considered for other land uses, such as agricultural activities which, locally, rely heavily on tile drainage. Such changes are of applied interest in terms of their impacts on hydrological functioning and how this affects stream water regimes, catchment storage and release of water in these landscapes.

Dominant soil types are brown soils on steeper slopes, podzols on gentler slopes and gleys and peats in low-lying areas, reflecting typical hydropedological sequences on Scottish hillslopes (cf. [22]). Topographically, the terrain is varied with elevation ranging from 32 to 335 m above sea level and average slopes of the study catchments ranging between 2.7° and 10.3° (Table 1). The climate is temperate with mean annual precipitation at ~950 mm and fairly constant potential evapotranspiration (PET) of around 500 mm. All areas drain towards the River Dee, which is the UK's largest unregulated river system. The Dee provides potable water to >300,000 people, sustains an economically important Atlantic salmon fishery and has high conservation value, meaning land use change decisions need to be informed in order to avoid adverse impacts.

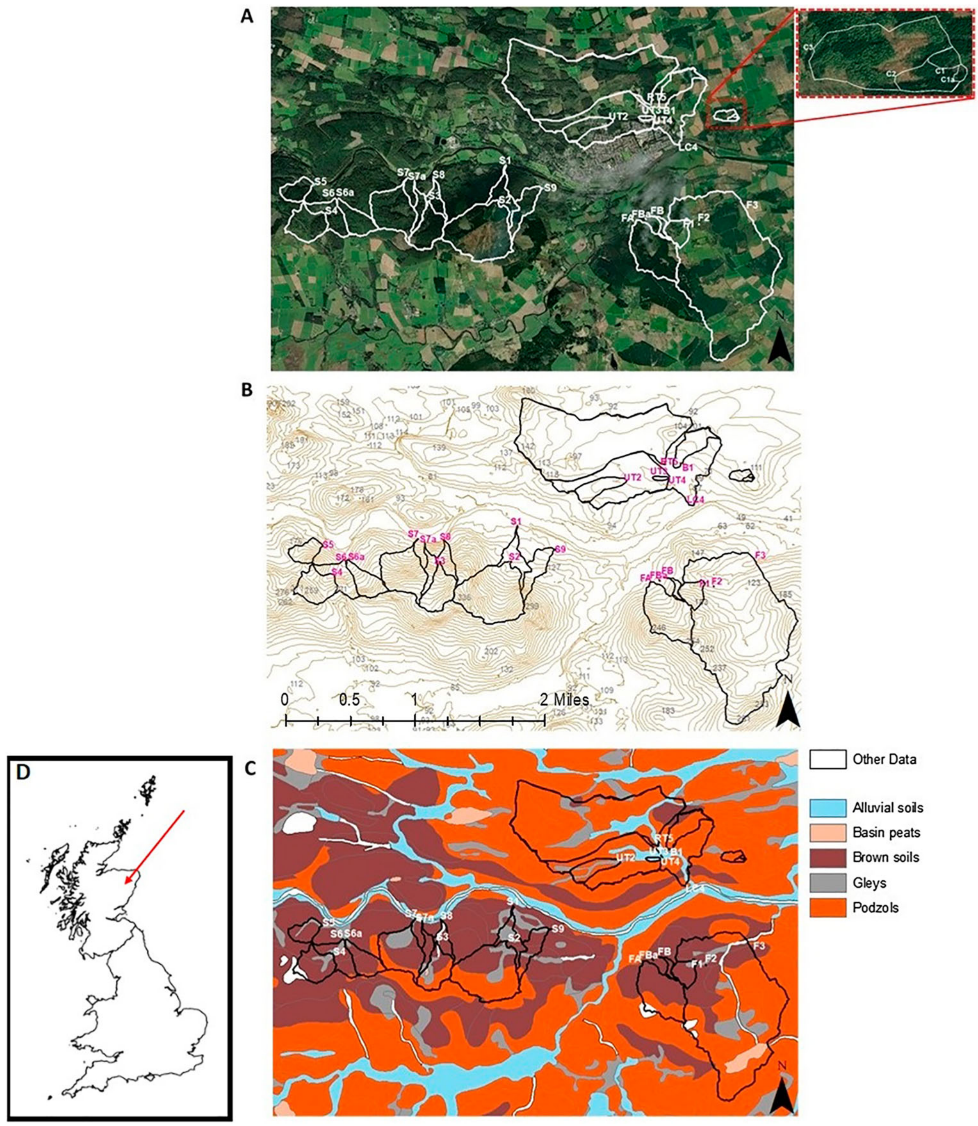

Figure 1. Aerial image providing an overview of study catchments land use (A), elevation contours in m (B), predominant soil types (C) and wider geographical reference (D). Daily precipitation samples were collected at the point denoted UT2.

3. Methodology

3.1. Data

We sampled 27 catchments within the study area, all of which were highly variable in size, proximity to the developing urban area, constituent rural land use and landscape characteristics (Table 1, Figure 1 and Figure 2). Five of the sites (LC4, RT5, UT2, UT3 and UT4) had been previously established by Soulsby et al. [23]. Stream water was sampled using grab sampling at the outlet of each catchment on a roughly fortnightly basis between October

Table 1. Catchment characteristics included in the construction on MLR models (prior to variable removal on the basis of multicollinearity).

Catchment	Size (km^2)	Soils of high responsiveness (%)	Freely draining soils (%)	Urban cover (%)	Agricultural cover (%)	Forest cover (%)	Mean slope (°)
LC4	6.50	84.0	16.0	16.1	35.2	48.7	3.0
RT5	4.54	84.3	15.7	1.0	27.7	71.3	3.3
UT2	0.34	100.0	0.0	63.3	0.0	36.7	3.2
UT3	1.69	87.8	12.2	12.4	59.0	28.6	2.8
UT4	0.03	17.4	82.6	100.0	0.0	0.0	5.8
B1	0.39	85.4	14.6	0.0	60.8	39.2	2.7
C1	0.006	100.0	0.0	0.0	0.0	100.0	2.7
C1A	0.002	100.0	0.0	0.0	0.0	100.0	10.3
C2	0.03	100.0	0.0	0.0	0.0	100.0	5.6
C3	0.11	100.0	0.0	0.0	0.0	100.0	6.4
F1	0.27	8.9	91.1	0.0	47.6	52.4	8.2
F2	0.0001	0.0	100.0	0.0	0.0	100.0	3.2
F3	6.45	70.5	29.5	0.0	48.2	51.8	5.6
FA	1.05	30.8	69.2	0.0	5.7	94.3	8.1
FB	0.06	0.0	100.0	0.0	17.0	83.0	7.2
FBa	0.0002	0.0	100.0	0.0	0.0	100.0	7.6
S1	1.90	62.0	38.0	0.0	0.0	100.0	9.1
S2	1.59	64.4	35.6	0.0	0.0	100.0	10.0
S3	0.52	68.7	31.3	0.0	0.0	100.0	8.7
S4	0.54	15.7	84.3	0.0	37.0	63.0	8.8
S5	0.27	17.5	82.5	0.0	0.0	100.0	9.7
S6	0.93	16.1	83.9	0.0	21.5	78.5	8.8
S6a	0.38	21.1	78.9	0.0	0.0	100.0	9.2
S7	0.88	47.2	52.8	0.0	0.0	100.0	10.1
S7a	0.17	18.5	81.5	0.0	0.0	100.0	9.4
S8	0.70	53.4	46.6	0.0	0.0	100.0	9.6
S9	0.35	26.9	73.1	0.0	0.0	100.0	7.0

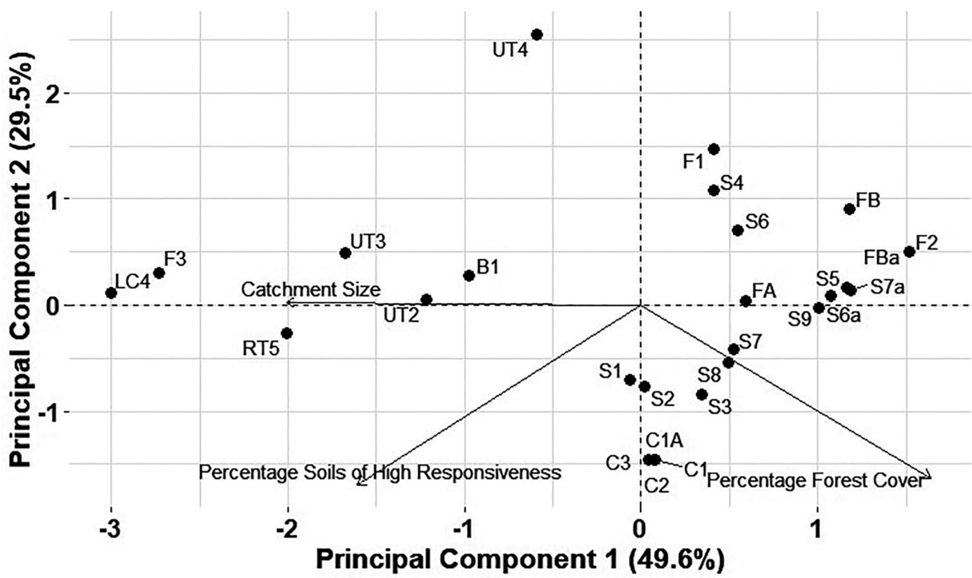

Figure 2. Principal component analysis using those variables included in the maximal MLR models (percentage of catchment forested, percentage of catchment having responsive soils and catchment size).

2013 and September 2014. This was considered a relatively 'low cost' sampling strategy that would be feasible as part of an environmental impact assessment or shorter-term low budget project where understanding hydrology was an important concept. However, within this temporal framework, efforts were made to target higher flow events; with the highest flows of winter and summer being captured at most sites. As part of a separate research project, daily precipitation isotope samples were collected near UT2 (Figure 1), in a sampler protected from evaporation. However, should such data not have been available it would have been possible to construct tentative precipitation isotope times series at monthly or even daily timesteps (cf. [24,25]) which would also facilitate aspects of the analysis described below. A single precipitation time series was deemed suitable given limited spatial variability in precipitation isotopes in the study area; previous work showed modest average elevation gradients (of around 2 and 0.2 ‰ per 100 m for δ^2H and $\delta^{18}O$, respectively) [26]. All stream water and precipitation samples were analysed for δ^2H and $\delta^{18}O$ at the University of Aberdeen using a Los Gatos DLT-100 laser isotope analyser (precision of ±0.4 ‰ for δ^2H and ±0.1 ‰ for $\delta^{18}O$); due to the higher relative precision, we used δ^2H in this study.

To determine daily amounts of precipitation, required for statistical analysis (see Section 3.2), an altitude-weighted nearest-neighbour analysis for five surrounding gauges was used. Modelled estimates of mean daily flows from the main urbanised catchment (LC4; Figure 1) were available to provide an index of flows in the general study area (refer to Soulsby et al. [23]). Such approaches to determine precipitation and streamflow were necessary mainly given the limited options to monitor these variables due to vandalism issues in urban areas. Further, we aimed at being consistent with the theme of a low resource study that can make valuable use of secondary hydrometric data sources and focused, limited data collection methods. We also utilised a seven-year daily precipitation, streamflow and PET dataset from a catchment ~30 miles away from the study area to help contextualise the study years hydroclimatic patterns in relation to other years, in an effort to aid interpretation of any results which could be influenced by the possible extreme nature of the study year. Specifically, we assessed how catchment storage levels (S) altered temporally across the study year in comparison to the longer-term average, via the following water balance equation:

$$S(t) = S(t-1) + P(t) - Q(t) - PET(t) \tag{1}$$

where t is the daily timestep, P is precipitation and Q is catchment discharge. For use within this metric, PET was assumed to be equal to actual evapotranspiration. S was reset to 0 on 1 October each year.

Catchments were delineated in ArcMap Desktop using a Digital Terrain Model supplied by Edina Digimap [27]. In smaller catchments, local site knowledge was used in some cases for minor adjustments of catchment boundaries. Land use was determined using GIS data supplied by Edina Digimap [28], with soil type data generated from maps supplied by the James Hutton Institute [29]. In line with previous studies (e.g. [30]), two soil classes were created: 'percentage soils of high responsiveness' (being dominated by surface and shallow sub-surface runoff generation processes when wet) and 'percentage freely draining soils' (being dominated by deeper sub-surface runoff generation processes and groundwater recharge) by grouping gleys, peats and podzols together and alluvial and brown soils, respectively (cf. [31]). Again, in smaller catchments local knowledge was used to enhance accuracy and validate the derived maps. Therefore, from the three GIS datasets seven catchment characteristics were estimated (Table 1), with these variables representing key influences on catchment hydrological function derived from readily available data.

The 27 catchments were split into three distinct geographical groupings; Scolty (catchments S in Figure 1), Feugh (catchments F in Figure 1) and Banchory and Crathes (catchments appended with the letters B, C, L, R and U in Figure 1). Catchment characteristics are summarised in Table 1, though in brief: the Scolty group consists predominantly of forested catchments with brown soils and steeper slopes, whilst the Feugh group have gentler slopes and increased agricultural presence. The Banchory and Crathes grouping is the most heterogeneous, encompassing the expanding town, mixed land use rural area and a range of soil types and slopes. This intra-geographical group heterogeneity is clearly represented in a principal component analysis (Figure 2). Furthermore, the Banchory and Crathes catchments are characteristically dissimilar to those within both the Scolty and Feugh groupings with the exception of F3, a catchment with relatively high agricultural presence. Clear outliers are also highlighted, specifically UT4, a small entirely urbanised catchment, as well as C1, C1A, C2 and C3 which cluster together away from other catchments, given their small size and complete forest cover.

3.2. Derivation of catchment functioning metrics

Three approaches were used to derive basic, yet informative, metrics of hydrological functioning from the isotope data. Firstly, the mean transit time (MTT; the average time a water molecule takes to travel through a catchment) for each catchment was calculated from a lumped convolution integral model (Equation (2)) using a gamma distribution (Equation (3)) as a transfer function.

$$\delta_{\text{out}}(t) = g(t) * \delta_{\text{in}}(t - \tau) = \int_0^\infty g(\tau)\delta_{\text{in}}(t - \tau)\mathrm{d}\tau \tag{2}$$

$$g(\tau) = \frac{\tau^{\alpha-1}}{\beta^{\alpha}{}_{\gamma}(\alpha)} \exp\left(-\frac{\tau}{\beta}\right) \tag{3}$$

The method converts the observed daily precipitation signal ($\delta_{\text{in}}(\text{t})$) into an approximation of observed stream water isotope signal ($\delta_{\text{out}}(t)$) using the described $g(\tau)$ function, where α and β represent shape (–) and scale (days) parameters, respectively. The scale parameter was restricted to a maximum of 1825 days given the limitations of stable isotopes to detect transit times above 5 years. To calibrate these parameters, we employed a differential evolution algorithm (DEoptim by Mullen et al. [32]) which optimised the modified Kling–Gupta efficiency (KGE; [33]) for fitting the stream isotope simulations. Fifty parameter sets were constrained over 100 generations to provide a final optimal parameter population of 100, which, in the absence of formal uncertainty analysis, provided some indication of the confidence interval estimates (plus and minus 1 standard deviation (SD)) around mean simulated values. Prior to each model run the timeseries in question was looped for two years to achieve an approximate mass balance prior to transit time calculation. Kirchner et al. [34,35] showed that the $g(\tau)$ function is generally the most appropriate way of characterising the transit time distribution (TTD) in catchments as it is able to capture both the short and long tails of the distribution, reflecting rapid and slower flow paths, respectively. The resulting MTT is a fundamental descriptor of catchment hydrological function [36] providing insight into the velocity of water movement through a catchment as a function of the interactions between storage and fluxes. It is derived from a simple model, is widely used, and thus has the potential to be informative in catchment management.

Secondly, the young water fraction [37,38] (YWF; stream water below a threshold age of around two to three months [39]) was calculated for each catchment, using volume-weighted precipitation and stream water isotope signals. This method uses the understanding that as water moves though a catchment and enters the stream there is a damping and phase shift of the original precipitation isotope signal. Sine wave fitting can then quantify this phase shift ($\phi_S - \phi_P$) and amplitude ratio (A_s/A_p) between the precipitation (Equation (4)) and stream water (Equation (5)) seasonal isotope cycles [39]:

$$c_P(t) = A_p \sin(2\pi f\ t - \phi_P) + k_p \tag{4}$$

$$c_s(t) = A_s \sin(2\pi f\ t - \phi_s) + k_s \tag{5}$$

where t is time in decimal years, A is amplitude (‰), ϕ represents (in radians, with 2π rad equalling 1 year) the phase of the seasonal cycle, f is the frequency (yr^{-1}), k (‰) is a constant detailing the vertical offset of the isotope signal and subscripts P and S refer to precipitation and stream water, respectively. The amplitudes A_p and A_s are estimated by using a multiple linear regression (MLR) to obtain coefficients of a and b in Equations (6) and (7):

$$c_P(t) = a_P \cos(2\pi f\ t) + b_P \sin(2\pi f\ t) + k_P \tag{6}$$

$$c_s(t) = a_s \cos(2\pi f\ t) + b_s \sin(2\pi f\ t) + k_s \tag{7}$$

As per, and using the R code provided in the supplementary material of, von Freyberg et al. [39], we used an iteratively re-weighted least-squares method to estimate the a_P, b_P, a_s and b_s coefficients. The amplitudes of A_s and A_p are then calculated via Equations (8) and (9), respectively, with the amplitude ratio then given by A_s/A_p [37–39].

$$\sqrt{a_P^2 + b_P^2} \tag{8}$$

$$\sqrt{a_S^2 + b_S^2} \tag{9}$$

The derived YWF can be complimentary to MTT by overcoming known limitations of MTT, such as fixed transit time distribution assumptions in catchments that are usually not in steady state, spatial aggregation errors and uncertainty over the longer tail of the distribution [37]. The YWF model is still relatively simple to apply with a computer code openly available via von Freyberg et al. [39].

Finally, the ratio of the standard deviation of stream water isotope samples to the standard deviation of precipitation isotope samples (hereafter S:P) was calculated for each catchment [40]. Smaller ratios indicate greater damping of the precipitation isotope signal and have been shown to be directly related to internal storage involved in mixing [41] and to have an inverse relationship with MTT values [42]. Our aim was to assess if these traits were present when using our low temporal frequency datasets, and if the S:P metric could be related to YWF, and thus provide a transferable tool for applied purposes.

3.3. Identification of potential landscape controls on catchment functioning metrics

A backward deletion approach to MLR was undertaken to assess which landscape characteristics were significantly related to MTT or YWF. MLR was only utilised for MTT and YWF as these statistics provided more quantitative metrics of catchment functioning, whilst the main reason for including the S:P was to test for a relationship with MTT and YWF. Backward deletion involves the initial inclusion of all potential explanatory variables within a 'maximal' MLR, with non-significant variables then removed iteratively until all remaining variables are statistically significant within the 'minimal' model. Before inclusion in the maximal model, variables detailed in Section 3.1 were tested for multi-collinearity to exclude those with a statistically significant relationship with another variable (s). Prior to multi-collinearity testing the variables MTT and catchment size were converted via natural logarithm given they spanned three and five orders of magnitude, respectively. Each datapoint was increased by one before conversion to avoid the generation of negative numbers for catchment size.

Multi-collinearity testing revealed percentage agricultural cover had a statistically significant relationship with percentage forest cover, average slope and catchment size, and so this was removed. Unsurprisingly, the two aggregated soil class percentages were also related. We therefore included the percentage soils of high responsiveness given that these would encourage more rapid runoff and likely generation of younger water in sampled streams. The inclusion of percentage soils of high responsiveness caused the exclusion of average slope. Finally, percentage urban cover and percentage forest cover were related, with the latter being more suitable for inclusion within the maximal model given that the former would include 22 zero values, potentially reducing information available to the analysis.

Consequently, the variables catchment size, percentage forest cover and percentage soils of high responsiveness were included in the maximal model. When a minimal model had been determined, model assumptions were checked to ensure statistical validity of the equation via normality testing of residuals, QQ plot inspection and quantification of Cooks distance; a metric used to identify influential outliers within regression analysis.

4. Results

4.1. Hydroclimate and isotope dynamics

The study year coincided with high levels of winter precipitation (Figure 3), indeed it was at the time the wettest UK winter on record [43], which resulted in very wet catchment conditions (Figure 4). The subsequent spring and summer were more typical, though still remained wetter than average years, with a wetter period also occurring in August 2014 (Figures 3 and 4). Precipitation isotope dynamics demonstrated strong seasonal changes, with heavily depleted values present during winter, which was clearly

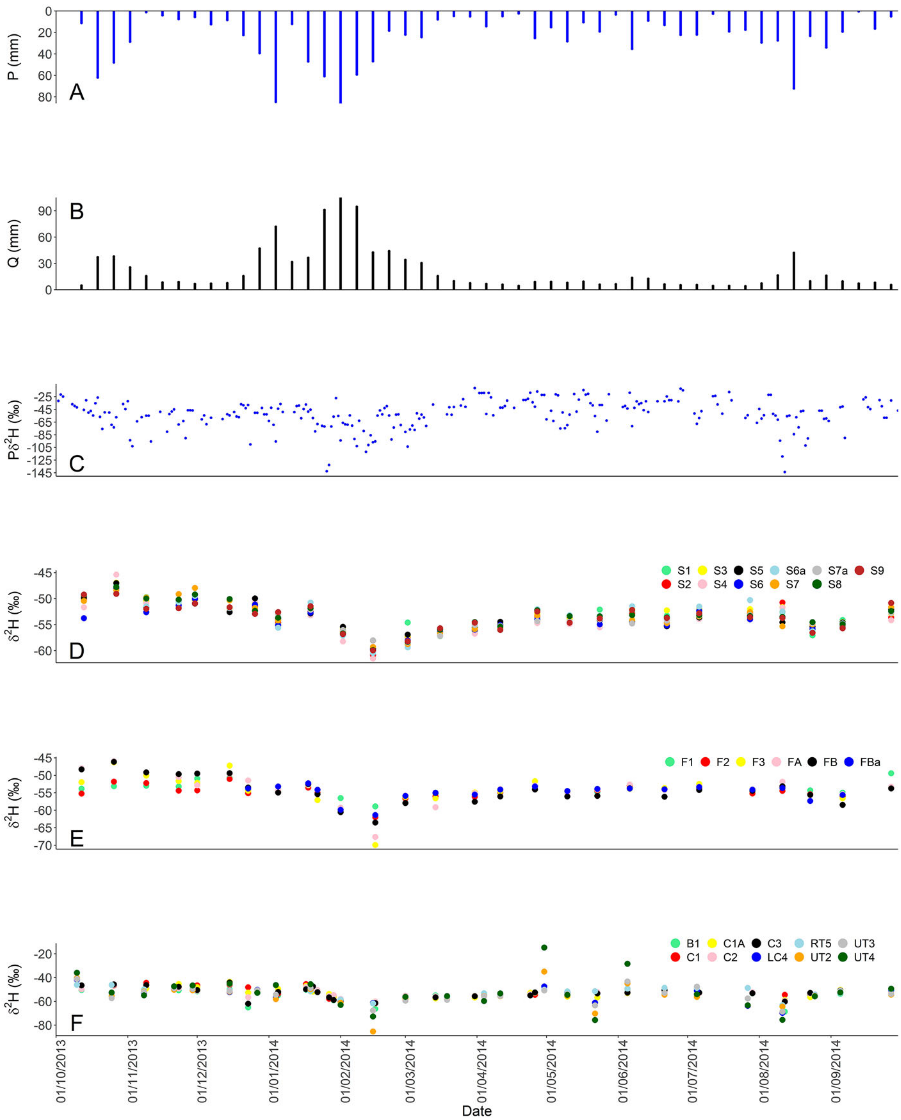

Figure 3. Weekly sum (date plotted plus total of previous six days) for precipitation (A), and streamflow at LC4 (B). δ^2H time series for precipitation (C), Scolty (D), Feugh (E) and Banchory and Crathes geographical groupings (F).

reflected in stream water signatures, though to differing extents. It should be noted that some variability will have inevitably been missed by the fortnightly sampling, though comparison with daily isotope data from a catchment 35 km away showed the main summer and winter variations were captured [44]. Highly urbanised catchments found within the Banchory and Crathes grouping, most obviously UT2 and UT4, showed a greater responsiveness to precipitation inputs with more limited damping. Notably, some catchments with larger proportions of agricultural land cover, such as UT3 and B1 within the Banchory and Crathes grouping and F3 from the Feugh grouping, also

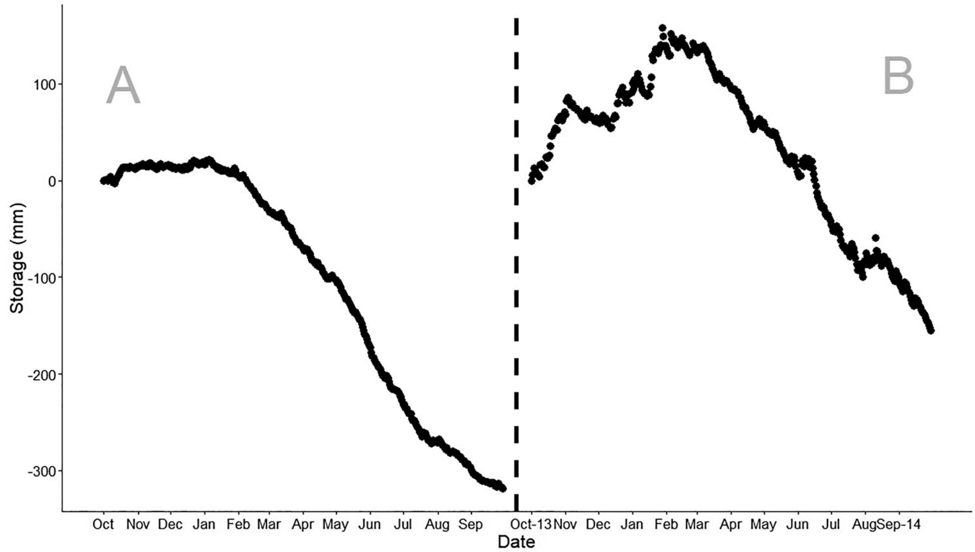

Figure 4. Regional water storage dynamic proxy, calculated as per Equation (1). Panel A displays the average daily value between 1 October 2011–30 September 2018. Panel B displays the daily value in the study year of 1 October 2013–30 September 2014.

demonstrated a relatively greater responsiveness to heavily depleted precipitation events (e.g. ~15 February 2014 in the stream water isotope time series; Figure 3) in comparison to other catchments within their respective groupings. Such dynamics were in contrast to the mostly forested catchments within the Scolty grouping which generally had the most damped range of all geographical groupings. Moreover, there was more limited intra-group variation in isotope dynamics within Scolty, with no individual catchment responding consistently differently to neighbouring sites. This consistency was further evident in dual isotope plots (Figure 5) where Scolty sites were most tightly clustered. In contrast, Banchory and Crathes had a much greater spread of data, whilst some values plotted below the Global Meteoric Water Line (GMWL) and precipitation derived Local Meteoric Water Line (LMWL; slope of 7.78 and intercept of 5.03) indicating evaporative fractionation effects [45].

4.2. Catchment functioning metrics

4.2.1. Mean transit time modelling

Transit time modelling resulted in tightly constrained MTT values for most sites, which spanned four orders of magnitude across all catchments (Figure 6 and Table 2), with predominantly aquifer supplied systems (e.g. FBa and F2) having the longest transit times. Those containing larger percentages of urbanisation, and thus impervious surface area, yielded the shortest MTTs (e.g. UT4 and UT2). On the whole, entirely forested catchments showed little intra-group variation in their predicted MTT, for example, C1, C1A, C2 and C3 within Banchory and Crathes and those catchments within the Scolty grouping, though with the notable exception of S7a, which was much higher. Such general consistency amongst forested catchments was directly contrasted to those with varying levels of

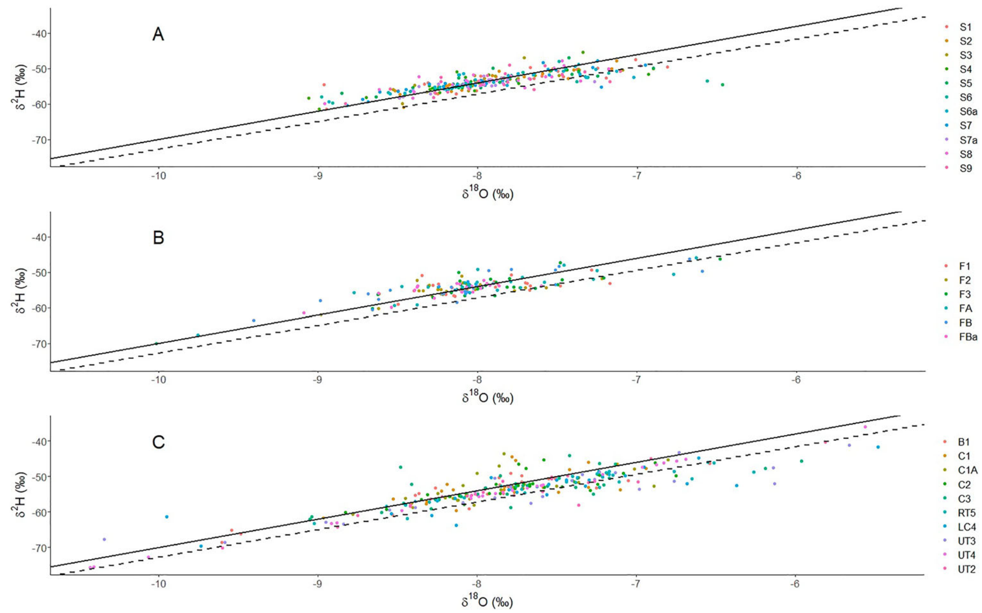

Figure 5. Dual isotope plots for the Scolty (A), Feugh (B) and Banchory and Crathes (C) groupings. To enable visual comparison between sites on the same axis scales one outlying data point from UT2 and two from UT4 were excluded. Solid lines indicate the Global Meteoric Waterline, dashed lines indicate the Local Meteoric Waterline.

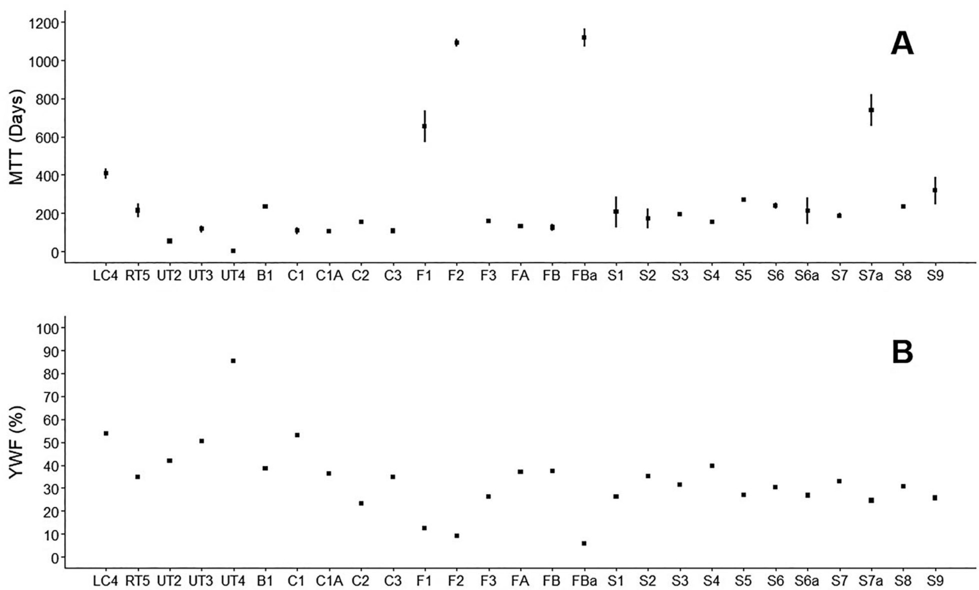

Figure 6. Simulated MTT (panel A; black square indicates mean value for MTT, black line indicates ± 1 SD) and YWF (panel B).

Table 2. MTT, modified Kling–Gupta efficiency statistics, α and β parameter values. Standard deviation (SD) confidence intervals calculated from the 100 retained parameter sets.

Catchment	Mean MTT + 1 SD (days)	Mean MTT (days)	Mean MTT − 1 SD (days)	Mean KGE + 1 SD (–)	Mean KGE (–)	Mean KGE 2– 1 SD (–)	Mean α + 1 SD(–)	Mean α (–)	Mean α − 1 SD (–)	Mean β + 1 SD (days)	Mean β (days)	Mean β − 1 SD (days)
LC4	435	407	380	0.68	0.68	0.68	0.23	0.23	0.22	1924	1789	1653
RT5	250	214	178	0.8	0.8	0.8	0.46	0.44	0.43	595	485	375
UT2	57	54	52	0.76	0.76	0.76	0.03	0.03	0.03	1868	1805	1741
UT3	135	118	100	0.78	0.78	0.78	0.33	0.32	0.30	475	376	278
UT4	3	1	0	0.65	0.65	0.65	0.02	0.02	−0.01	88	81	73
B1	241	233	226	0.59	0.59	0.59	0.36	0.36	0.35	680	653	626
C1	126	108	91	0.78	0.77	0.77	0.85	0.80	0.76	179	137	96
C1A	105	104	102	0.74	0.74	0.74	0.85	0.83	0.82	129	125	121
C2	161	155	150	0.71	0.71	0.71	0.77	0.76	0.74	217	205	193
C3	115	107	100	0.65	0.65	0.65	0.76	0.73	0.70	166	147	129
F1	738	655	571	0.66	0.66	0.66	0.73	0.72	0.70	1055	916	778
F2	1114	1092	1071	0.65	0.65	0.65	0.60	0.60	0.60	1852	1816	1781
F3	163	159	155	0.62	0.62	0.62	0.60	0.59	0.58	281	271	260
FA	137	132	126	0.68	0.68	0.67	0.75	0.73	0.72	192	180	168
FB	142	125	108	0.66	0.65	0.65	0.94	0.89	0.83	192	144	97
FBa	1167	1120	1073	0.68	0.68	0.68	0.62	0.62	0.62	1888	1808	1727
S1	288	206	125	0.74	0.74	0.74	0.84	0.80	0.76	437	267	97
S2	225	173	121	0.76	0.75	0.74	0.99	0.94	0.88	294	191	88
S3	201	193	186	0.74	0.74	0.74	0.89	0.88	0.86	234	221	207
S4	159	153	147	0.71	0.71	0.71	0.96	0.94	0.92	173	163	153
S5	278	270	261	0.74	0.74	0.74	0.82	0.81	0.80	347	333	318
S6	255	239	223	0.74	0.74	0.74	0.88	0.85	0.83	311	281	250
S6a	282	212	143	0.78	0.77	0.77	0.81	0.78	0.74	420	279	139
S7	203	187	172	0.79	0.79	0.79	0.86	0.84	0.82	253	224	194
S7a	821	738	655	0.85	0.85	0.85	0.77	0.76	0.75	1102	974	845
S8	236	234	231	0.76	0.76	0.76	0.77	0.76	0.76	311	306	302
S9	388	318	247	0.79	0.79	0.79	0.73	0.71	0.70	581	448	315

more intense anthropogenic disturbance within the Banchory and Crathes grouping (in terms of urbanisation and agricultural presence) where B1, LC4, RT5, UT2, UT3 and UT4 had relatively high divergence in their respective MTT estimates.

Analysis of MTT fitting parameter values (Table 2) also showed these catchments had lower mean α parameters in comparison to all other catchments in the study. A lower α parameter indicates a more pronounced initial tracer peak and longer tail to the TTD [46], meaning catchments were weighted to faster transit times. Consideration of the α parameter, therefore, can potentially give further insight into the mechanisms behind a catchment's MTT as this value is derived from integration of the TTD, rather than simply the peak of tracer recovery. Given B1, LC4, RT5, UT2, UT3 and UT4 were characterised by more intense (relative to forested areas) levels of anthropogenic disturbance through increased agriculture and urbanisation presence, we hypothesised this may be reflected in the α parameter. Therefore, as an additional test we grouped percentage agricultural cover and percentage urban cover together in one individual class and undertook a linear regression against the mean α parameter to investigate this. A significant and relatively strong, negative relationship was observed ($R^2 = 0.61$, $P \leq 0.001$; Figure 7) indicating that catchments containing higher levels of forestry were more likely to have longer times until the peak of the TTD occurred, whereas more anthropogenically disturbed catchments had a greater tendency to shorter TTD peaks.

4.2.2. Young water fractions

YWF estimates (Figure 6 and Table 3) had many features that would be expected, with the largest fraction being observed in the highly urbanised, small catchment of UT4 and the lowest being in that of the predominantly aquifer fed FBa. Banchory and Crathes catchments again showed relatively greater variation in their YWF estimates, reflecting the diversity of land uses, whilst Scolty catchments remained fairly consistent given their relatively homogenous levels of forest cover. Across all 27 catchments, YWF values had a significant, moderate negative relationship with MTT estimates ($R^2 = 0.40$, $P \leq 0.05$). However, when considering individual geographical groupings there was more obvious divergences between MTT and YWF. These differences were most notable in the Banchory and Crathes groupings (Figure 6), possibly a result of fractionation occurring within

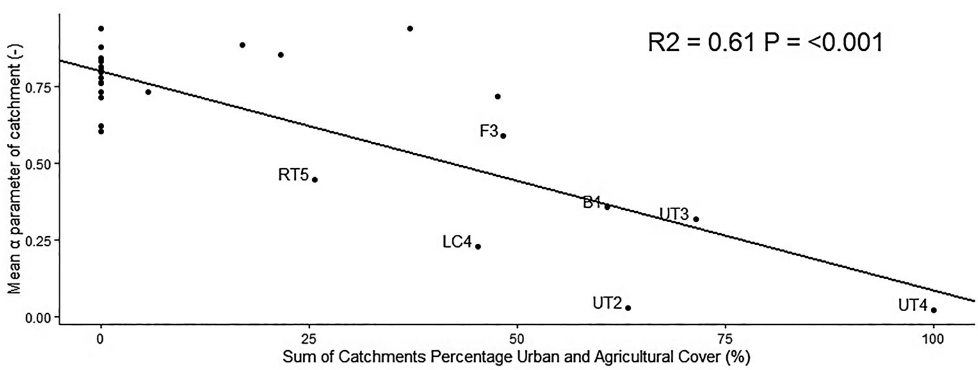

Figure 7. Linear regression between mean catchment α parameter values and sum of catchments urban and agricultural cover. Points labelled are those with an alpha parameter of <0.60.

Table 3. YWF values and the ratio of the standard deviation of streamflow isotope samples to the standard deviation of precipitation isotope samples (S:P).

Catchment	YWF	S:P
LC4	53.9	0.26
RT5	34.7	0.19
UT2	41.9	0.41
UT3	50.3	0.28
UT4	85.5	0.58
B1	38.4	0.22
C1	53.1	0.19
C1A	36.4	0.19
C2	23.3	0.15
C3	34.9	0.20
F1	12.4	0.08
F2	9	0.10
F3	26.1	0.18
FA	36.9	0.17
FB	37.5	0.17
FBa	5.7	0.10
S1	26.3	0.13
S2	35.2	0.13
S3	31.4	0.12
S4	39.7	0.14
S5	26.9	0.10
S6	30.2	0.11
S6a	26.8	0.13
S7	32.9	0.13
S7a	24.6	0.07
S8	30.7	0.12
S9	25.7	0.11

wetlands that are present within the area. In contrast to Banchory and Crathes, Feugh catchments showed a strong negative relationship between YWF and MTT values ($R^2 = 0.86$, $P \leq 0.05$). YWF also exhibited a significant, though weak, negative relationship with the MTT α parameters ($R^2 = 0.23$, $P \leq 0.05$). This reflected individual catchments (e.g. LC4 and B1) containing relatively larger extents of urbanisation and agriculture, and so lower α values, also having higher YWF, though there was a great deal of scatter in the relationship.

4.2.3. S:P ratio

The S:P ratios (Table 3) were largest for the catchments with lower MTT and higher YWF (e.g. UT4 and UT2), whilst smaller ratios were calculated for the catchments dominated by groundwater such as S7a and F1. Given this, S:P values had a significant negative relationship with MTT and significant positive relationship with YWF statistics ($R^2 = 0.70$ and 0.68, respectively, with $P \leq 0.05$; Figure 8). The S:P values were also able to highlight outliers within geographical groupings, such as catchment S7a within the Scolty grouping which also had a high MTT estimate in comparison to other catchments within the grouping. Furthermore, the S:P ratios also ranked the mixed land use catchments from Banchory and Crathes (LC4, RT5, UT2, UT3 and B1) as having some of the largest ratios, indicating a relatively reduced damping of the isotope signal and therefore more rapid transfer of precipitation to stream water, which is consistent with the α parameters (Table 2 and Figure 7).

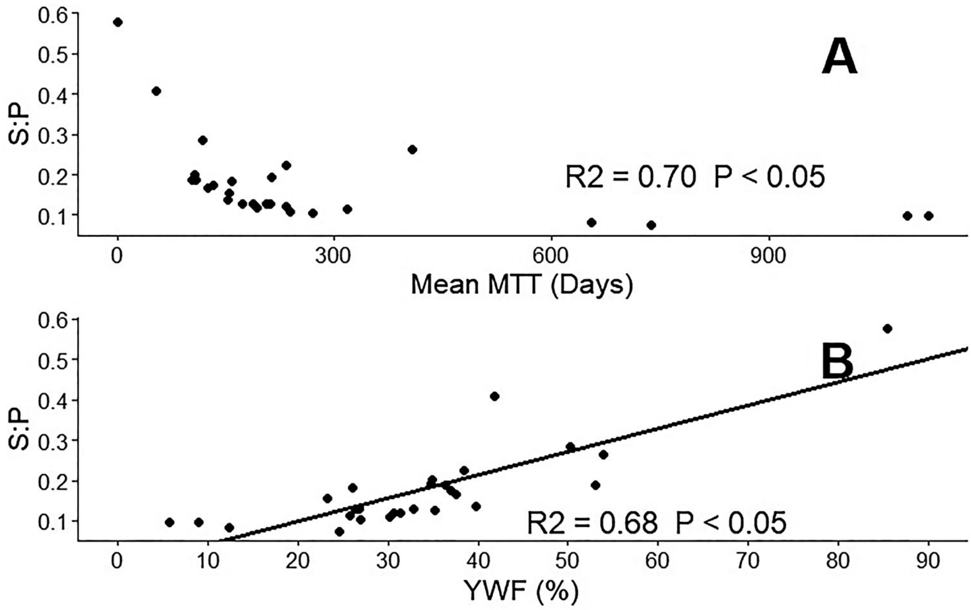

Figure 8. Relationship between the SD of streamflow isotopes relative to that in precipitation isotopes and mean MTT or YWF (panels A and B, respectively). Note, no line of best fit is included in panel A as the relationship calculated was done so using logarithmically converted MTT values, the displaying of which would provide less intuitive *x*-axis values.

4.3. Multiple linear regression analysis

4.3.1. Mean transit time minimal model

The minimal model (see Section 3.3 and Figure 9 for definition) for predicting MTT values included percentage soils of high responsiveness and percentage forest cover, including interaction terms between variables, with an R^2 of 0.54 ($P \leq 0.05$). All variables within the model were also individually statistically significant ($P \leq 0.001$). However, model assumption testing revealed that UT4 was heavily influential in terms of Cook's distance. When the site was excluded in re-analysis, catchment size had to be excluded from the maximal model due to a statistically significant interaction with percentage forest cover. The minimal model again included percentage soils of high responsiveness and percentage forest cover (including interaction terms). Despite this minimal model being statistically significant overall ($P \leq 0.05$), none of the variables within the model were, whilst the explanatory power of the model was reduced ($R^2 = 0.33$). Inspection of the raw data (Table 1, Figures 2 and 3) evidenced that the UT4 datapoint was a clear outlier in comparison to other catchments given its small size, extreme urbanisation and very low MTT. Thus, the site had a high information content and its inclusion facilitated a much improved model fit through forcing the regression lines and better capturing the tails of the MTT distribution. Consequently, the site was retained in the final MLR, though interpretations need to be suitably circumspect.

4.3.2. Young water fraction minimal model

The minimal model for YWF also included percentage soils of high responsiveness and percentage forest cover (including interaction terms), with a similar R^2 of 0.49 and

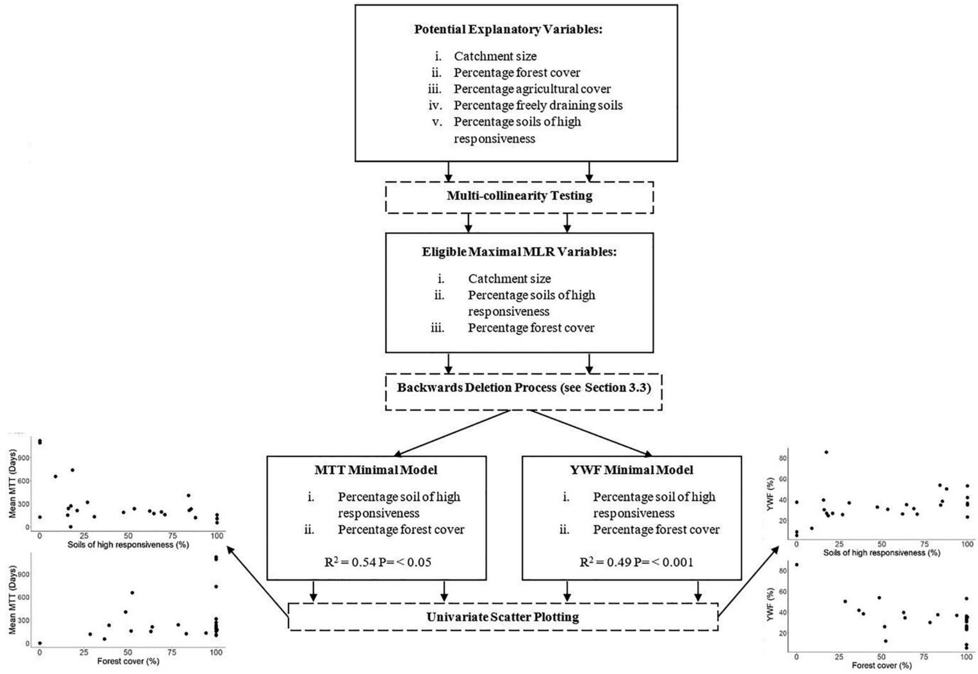

Figure 9. Schematic summary of derived minimal MLR models and univariate plots of retained explanatory variables. Refer to Sections 3.3 and 4.3 for full details on the process to ascertain displayed minimal models.

overall model *P* value of <0.001. Here, the variable of percentage soils of high responsiveness was only statistically significant within the interaction term. Again, UT4 was trial removed given its Cook's distance, however once more this caused a collapse of all variables significance within the model and reduced the models explanatory power and therefore the datapoint was retained.

5. Discussion

5.1. Identifying local differences in catchment functioning through a reconnaissance style isotope sampling approach

In this study, we sampled 27 stream waters for isotopic analysis over one year on a roughly fortnightly basis within and surrounding a rapidly growing town with a rural hinterland which had both agricultural management and mature forestry plantations. This was to ascertain if such an approach, accompanied with available auxiliary data, could be used to identify heterogeneities in catchment functioning and the dominant controls on hydrological processes.

The resulting isotope data allowed us to identify fundamental differences in catchment hydrological functioning across geographical groupings via simple MTT or YWF models. Results distinguished those catchments with greater coverage of urbanisation (e.g. UT4 and UT2) which has been shown to reduce transit times in the local area to days or weeks [47] and those streams predominantly fed by local aquifers (e.g. FBa) where YWF would be lower and MTT would expected to be longer, in the order of years (cf. [48,49]). Within geographical groupings, we were also able to identify catchments with fundamentally different MTT and YWF to contiguous catchments, such as F1, F2 and FBa having high MTT and low YWF in comparison to their neighbouring catchments. Not only did this provide insight into hydrological regime heterogeneities within the local landscape but it also helped increase confidence in results which indicated less intra-group differences in MTT and YWF (such as C1, C1A, C2 and C3) and thus identify landscape areas more homogenous in hydrological functioning. Furthermore, analysis of the MTT α parameter allowed us to understand which catchments within and between geographical groupings were more likely to have TTD biased to faster transit times.

The isotope data could also be successfully applied to generate simple S:P ratios which were significantly related to MTT and YWF. Though previous studies (e.g. [40–42]) have shown this to be the case for MTT, we were able to demonstrate how low frequency sampling at high spatial density can also generate simple statistics which can be related to the YWF. The S:P metric avoids some of the assumptions and uncertainties of MTT (see Section 3.2) and has the potential to be simplified further by only comparing the inter-catchment standard deviation of stream water isotope signal should a precipitation isotope time series not be available. The information content of the S:P ratio was specifically demonstrated when considering, for example, that the S:P values ranked LC4, RT5, UT2, UT3 and B1 as having limited damping, therefore inferring lower storage and more rapid transfer of precipitation to stream water, as was inferred by analysis of the TTD distribution via the α parameter and broadly corroborated by the YWF values.

5.2. Identifying dominant landscape controls on hydrological functioning

Results from MLR analysis (Section 4.3 and Figure 9) showed that in the study catchments percentage soils of high responsiveness and percentage forest cover were key predictors of both MTT and YWF. Previous studies in Scotland [30,50] have shown responsive soils such as peats and gleys tend to reduce MTT through faster lateral movement of water to the stream via saturation overland flow, which would also lead to higher YWFs. Conversely, forest cover tends to be on freer draining soils which will encourage groundwater recharge, whilst the canopy cover can attenuate flow through interception and transpiration, though the extent of this is dependent on forest characteristics (e.g. species, age, canopy structure and position in the landscape [51,52]). However, strong co-linearity in many catchment characteristics dictate that these two variables are potentially proxy for other drivers of hydrological function, either those removed from MLR or where data was not available. In addition, the MLR has a multi-dimensional plane which includes interaction terms between variables. However, univariate scatter plots (Figure 9) highlight the directional changes to MTT and YWF by percentage soils of high responsiveness and percentage forest cover, albeit with considerable scatter. Despite these complexities, our results do show that reconnaissance style isotope sampling in conjunction with MLR modelling can identify differences in landscape controls that are intuitively influential in catchment hydrological functioning.

Furthermore, analysis of the MTT α parameter revealed that as the relative intensity of anthropogenic disturbance increases (through agriculture and urbanisation), the impact of younger water on stream water increases (Figure 7). Within an urban environment, this would be expected given increases of impervious surface area which can reduce precipitation infiltration and increase event runoff via urban storm drains [10,53], whilst agricultural practices can have similar effects through soil compaction [12]. Finally, our analysis further demonstrated the importance of including within reconnaissance style isotope sampling catchments which characterise the tails of MTT and YWF distributions. For example, data collected from the only entirely urbanised, and small catchment (UT4) was shown to have high information content which helped to improve model fit and general hydrological understanding at the landscape scale in Section 4.3. Inclusion of other catchments with outlying characteristics, such as the predominantly groundwater fed, entirely forested FBa, will have further helped our dataset capture differences of landscape catchment functioning, given they capture dynamics which may be lost within larger catchments as landscape heterogeneity would damp out their contribution to MTTs and YWFs.

5.3. Limitations of reconnaissance style stream water isotope sampling for applied use

Isotopes have clear potential to aid decision makers assessing the impact of land use change to hydrological regimes. This is due to their ability to aid understanding of hydrological functioning at the catchment scale [5], though how to balance resource efficiency and dataset information content is an open question [15]. Our reconnaissance style sampling could identify both inter- and intra-geographical differences in hydrological functioning, even in its simplest form where differences in stream water isotope damping were indicative of catchments more rapidly cycling precipitation inputs to stream water (e.g. UT4 and B1; Figure 3). Visual examination further revealed that more urban and agriculture influenced catchments were relatively more responsive than forested areas, an intuitive conclusion given forest loss has globally been associated with runoff increases (cf. [54]). Such results demonstrate derived datasets do not necessarily require excessive time resources for interpretation, enabling them to compliment, not hinder, other sources of hydrological information a decision maker will acquire.

Indeed, application of the basic S:P metric, which could be calculated quickly through simple spreadsheets (and could feasibly be simplified further by only considering the standard deviation of stream water), highlighted informative inter-catchment differences which correlated to the more quantifiable MTT and YWF values. Again, models that derived MTTs and YWFs are relatively simple to apply, with computer codes freely available (for example YWF code is available via von Freyberg et al. [39]). This enables them to be both time and resource efficient, thereby not detracting resources from other environmental considerations, and yield process-based insights into catchment functioning which could aid land use change decision making. For example, we found catchments within geographical groupings which had fundamentally different MTT and YWF to their contiguous counterparts (such as such as F1, F2 and FBa having high MTT and low YWF in comparison to neighbouring catchments). This means the data has substantial value in aiding land use change decisions as it highlights areas of the landscape which are relatively more active in routing precipitation to groundwater. Therefore, land use alterations which can directly impact groundwater recharge may have a greater impact on hydrological function within these areas.

Information on MTTs and YWFs could also be useful in terms of better highlighting potential pollution risk within a landscape and thus areas more susceptible to rapid transport of pollution to stream water, contamination of groundwater and help identify potential mitigation measures [20]. Such examples demonstrate how reconnaissance isotope sampling can complement and build upon other methods of hydrological investigation, such as detailed spatial analysis to gain insight into possible hydrological functioning. The data does this through providing a relatively fine scale and quantifiable, local, process-based perspective on hydrological function within landscape compartments. The fact that conclusions are drawn from locally derived data is also important in ensuring datasets could be successfully utilised to define and defend decisions on land use change. For instance, analysis of the MTT α parameter and MLR demonstrated how forestry attenuates precipitation transfer to stream water, whilst urbanisation and agriculture have a reverse effect *within* this local landscape, rather than relying on inferences from case studies elsewhere.

Clearly, however, there are clear limitations to such an isotope sampling approach which must be considered. Firstly, the datasets are not capturing stream samples under the full range of high flow conditions, principally driven by precipitation events. Although the highest summer and winter events were sampled, the under-representation of high flows are likely to effect (increase) the resulting MTT estimates, though the effect would be similar amongst most of the catchments sampled. In addition, it should be stressed that even sampling over one year will be insufficient to fully characterise the MTT [22], given that TTDs are inherently time variable [55] with hydroclimate and antecedent conditions meaning that the MTTs should be viewed tentatively as a first approximations that mainly highlight inter-catchment differences. It is also inevitable that one-year low frequency sampling will miss hydrological extremes that are important for characterising a catchment's response to flood and drought events that are likely to become more common under a changing climate and would therefore be of interest to environmental managers. However, a reconnaissance style approach could be adapted to include auxiliary collection of high flow events, though in our case sampling already captured some of these. Criticism could also be present around results being able to be deduced *a priori*, without the allocation of resources to isotope data collection, specifically in relation to identifying dominant landscape controls on hydrological functioning. However, our application of isotope data should be viewed as providing more process-based understanding of the landscape at relatively high spatial resolution, without relying on inferences drawn from studies conducted elsewhere. In this sense, data and insights from stable water isotopes can be a valuable addition to tools available for decision makers.

6. Conclusion

We adopted a roughly two-weekly frequency to stream water sampling for isotopic analysis in 27 locations over one year in a local area in NE Scotland undergoing rapid land use change. This aimed to investigate if such an approach could identify inter-catchment differences in hydrological function and the associated landscape controls, thereby aiding understanding of how land use change may impact hydrological regimes. The approach yielded datasets that enabled relatively constrained first approximations of

MTT and broadly consistent estimates of YWF, which could identify heterogeneities and similarities in catchment functioning within and between distinct geographical groupings. The data could also be applied to generate statistical metric of stream water isotope variability (S:P) which was shown to be strongly correlated with both MTT and YWFs. Moreover, the datasets were able to help identify the general catchment characteristics controlling catchment functioning; urbanisation, agricultural activities and responsive soil cover increased the rate of precipitation transfer to stream water, whilst forest cover attenuated this. Drawbacks were present around the study only capturing catchment functioning during an extreme wet year.

Nonetheless, the results clearly demonstrate that such a sampling approach can be viewed as a useful, low resource, tool for decision makers which provides locally specific, process-based information that can complement other sources of hydrological information. Future work could replicate the study in an area of fundamentally different catchment characteristics to determine if the approach is fully transferable to other geographical locations.

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